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SYNTHESIS OF 3-(POLYFLUOROALKYL)PYRAZOL-4-AMINES ON THE BASIS OF LITHIUM 1,3-DIKETONATES*

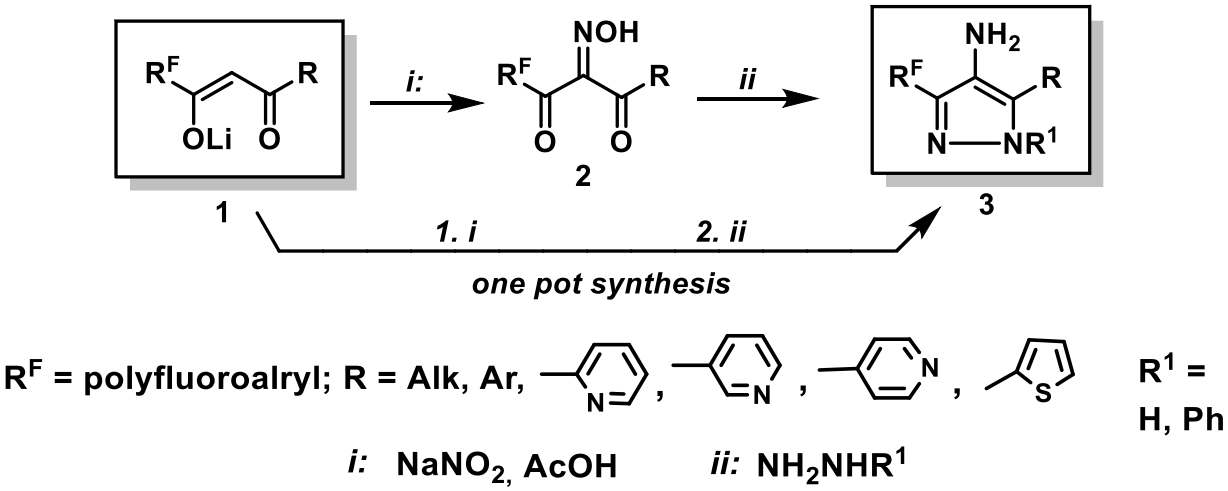
Keywords: lithium 3-polyfluoroalkyl-1,3-diketonates, hydrazine hydrate, 3-(polyfluoroalkyl)-4-aminopyrazoles.

Fluoroalkyl-containing pyrazoles are important building blocks for the synthesis of biologically active compounds and a variety of coordination compounds. Indeed, effective anti-inflammatory drugs, such as celebrex or celecoxib, and the veterinary anti-arthritic agent mavacoxib (troxoxyl) contain the (trifluoromethyl)-pyrazole fragment in their structures [1, 2]. The incorporation of functional groups into the pyrazole ring expands synthetic opportunities for modification of these compounds. For example, due to the presence of NH_2-group in 5-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-4-amine, new derivatives bearing fragments of 3-trifluoromethylpyrazole and 1,2,3-triazole have been obtained. These compounds proved to exhibit a cytotoxicity against lung cancer cells and antimycobacterial activity against *Mycobacterium smegmatis* [3]. However, the known methods to obtain 3-(polyfluoroalkyl)-4-aminopyrazoles involve several laborious operations and require isolation of the intermediates [3, 4].

In this communication we wish to report on the developed *step by step* and *one pot* syntheses of 3-(polyfluoroalkyl)-4-aminopyrazoles **3** starting from the readily available lithium 1,3-diketonates **1**.

Step by step method 1. Nitrosation of 1,3-diketonates **1** results in the corresponding oximes **2** [5]. Treatment of compounds **2** with hydrazine yields the required 4-aminopyrazoles **3**.

One pot method 2. Treatment of diketonates **1** with sodium nitrite in acetic acid, followed by the reaction with hydrazines, proceeding without isolation of intermediate oximes **2**. [6].



The preparation of 4-aminopyrazoles **3** is a simple method, providing good yields of the target products in the range of 65-95%. Products **3** have been characterized by the data of elementary analysis, GC-MS, IR, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

Reducing a number of operations associated with the synthesis and separation of oximes **2**, leads to a significant saving of time, reagents, and minimization of waste. We believe that the proposed *one pot protocol* meets the principles of "green chemistry".

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